ON THE BASIC NITROGEN COMPOUNDS FROM FUSHUN SHALE TAR. II.

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(*Continued from the last page*).

2 : 3 : 5–Trimethylpyridine. The writer has succeeded in isolating 2 : 3 : 5–trimethylpyridine, a new base, as one of the chief constituents in the fraction of 186°–190°, which has never been before submitted to a satisfactory investigation and forms the sixth upheaval in the fractionation curve, (cf. previous report p. 179).

The fraction (71 gr.) was treated with the calculated amount of picric acid, in an alcohol solution, and the crystalline picrate was collected, and yielded 30 gr. of the free base. The base was again treated with an insufficient quantity of picric acid in an excess of alcohol out of which the picrate was produced in the form of cilia first which melts at 184° after purification.

Twenty one gr. of the purified picrate gave 6.8 gr. of the base with a faint agreeable odour resembling 3 : 5–dimethylpyridine in a way. The boiling point of the dried base over fused potash remained constant during the distillation at 186.75° (761.1 mm.).

The constants are ; $d_4^{25}=0.9310$ (in vac.) ; $n_D^{25}=1.5057$; $n_C^{25}=1.5014$; $n_F^{25}=1.5171$; $n_G^{25}=1.5270$.

$(C_8H_{11}N\cdot HCl)_2PtCl_4$ . . . . . an orange-red prism, m.p. 212°. (0.1032 Gr. subst. gave 0.0297 gr. Pt. Found Pt=28.8, theoretical Pt=28.7%).

$C_8H_{11}N\cdot HCl\cdot 3HgCl_2$ . . . . . needles ; soluble in hot, slightly in cold water ; m.p. 110°.

Picrate . . . . . a needle from hot alcohol ; slightly soluble even in hot alcohol.

0.1016 Gr. base gave 0.0830 gr. H_2O and 0.2954 gr. CO_2. 0.1872 Gr. base gave 19.3 c.c. N_2 at 26° and 757 mm. (Found : C=79.29 ; H=9.15 ; N=11.73. $C_8H_{11}N$ requires C=79.27 ; H=9.16 ; N=11.56 %).

1.3 Gr. of the base was oxidised with potassium permanganate and the oxidation product was purified as a silver salt, and decomposed with hydrogen sulphide, yielding 1.5 gr. of the free acid.

The free acid is easily soluble in hot water, but not in cold, crystallizes out from water as white granules ; melts at 320°–322° with decomposition, and becomes deep orange-red with ferrous sulphate. The analysis and

properties of the free acid agree well with those of 2 : 3 : 5–pyridinetricarboxilic acid.[1]

0.1452 Gr. free acid lost 0.0200 gr. on drying at 110° for 2 hours. To neutralise 0.1013 gr. of free acid required 12.5 c.c. of N/10 NaOH using phenolphthalein as indicator. 0.1127 Gr. dried acid gave 0.0290 gr. H_2O and 0.1862 gr. CO_2. (Found : water of crystallization = 13.77 ; C = 45.06 ; H = 2.88 ; mol. wt. = 243. $C_5H_2N\cdot(CO_2H)_3\,2H_2O$ requires water of crystallization = 14.58 ; C = 45.49 ; H = 2.39% ; mol. wt. = 247).

2 : 4 : 5–Trimethylpyridine.[2] In view of a certain relationship among the boiling-points of the methyl-pyridines which was stated above, we can assume that among the trimethylpyridines, 2 : 3 : 4–, 2 : 3 : 5–, and 2 : 4 : 5–methyl pyridines would exist in the fraction of b. p. 186°–190°, and the last two substances have been isolated.

By treating the fraction with picric acid 2 : 3 : 5–collidine was separated out in ciliform-like crystals (cf. former section) and then, the scaly crystals of 2 : 4 : 5–trimethyl pyridine appeared polluted by the former, which transformed gradually into thick plates in alcohol and could be readily separated from the latter mechanically by decantation. The melting-point of the picrate, on purifying from the alcohol solution, showed constant at 161° and the yield was 29 gr.

The base has a characteristic odour like the kidney-bean, and is soluble in 50 parts of water at 25°. The dried base completely distils at 190.04°–190.05° under 766. 1 mm. and has the constants : $d_4^{25} = 0.9330$ (in vac.) ; $n_D^{25} = 1.5054$; $n_C^{25} = 1.5013$; $n_F^{25} = 1.5165$; $n_{G'}^{25} = 1.5260$.

$(C_8H_{11}N\cdot HCl)_2PtCl_4$ . . . . . needles, m.p. 192°

$C_8H_{11}N\cdot HCl\cdot 3HgCl_2\cdot 2H_2O$ . . glass-wool-like needles, m.p. 112° (Hg found = 59.5 ; theory = 59.7%)

0.1067 Gr. of the base gave 0.0875 gr. H_2O and 0.3107 gr. CO_2. 0.1900 Gr. base gave 19.3 c.c. N_2 at 25° and 759 mm. (Found : C = 79.42 ; H = 9.18 ; N = 11.63 ; mol. wt. = 121. $C_8H_{11}N$ requires C = 79.27 ; H = 9.16 ; N = 11.56% ; mol. wt. = 121.1).

The base (1.2 gr.), on oxidation with potassium permanganate solution yielded 1.6 gr. of free acid (m.p. 244°) which was ascertained to be "berberonic acid"[3] from its form, solubility in water and colour reaction toward ferrous sulphate.

To neutralise 0.1017 gr. of free acid required 12.2 c.c. N/10 NaOH. 0.1629 Gr. free acid lost 0.0221 gr. on drying at 96° for 3 hours. 0.1065 Gr. dried acid gave 0.0235 gr. H_2O and 0.1775 gr. CO_2. (Found : water of

(1) E. Dürkopf and M. Schlaugk, *Ber.*, **21** (1888), 835.
(2) F.B. Ahrens, *Ber.*, **29** (1896), 2999.
(3) O. Mumm and H. Hüneke, *Ber.*, **51** (1918), 150.

crystallization = 13.56 ; C = 45.46 ; H = 2.47 ; mol. wt. = 250. $C_5H_2N\cdot(CO_2H)_3\cdot 2H_2O$ requires H_2O = 14.58 ; C = 45.49 ; H = 2.39% ; mol. wt. = 247).

2 : 3 : 4 : 6–Tetramethylpyridine. It was assumed that the two isomers of tetramethylpyridine, (2 : 3 : 4 : 6– and 2 : 3 : 5 : 6–) would occur in the last fraction b.p. 200°–202°.

On treating the base of this portion with picric acid in an alcohol solution, crystalline and amorphous picrates were obtained. The amorphous picrate was extremely soluble even in cold alcohol, but only slightly in hot water, and this picrate on decomposition with alkali liberated a colourless base of a strong offensive odour. It was neutralised with a very dilute hydrochloric acid and when treated with picric acid, a brownish-red oily picrate was deposited, which on standing for a week or so, was gradually transformed into pale yellow fur-like crystals, and on being purified from a dilute methyl alcohol solution, the yield of pure picrate (m p. 107°) was 18 gr.

The free base is a hygroscopic colourless liquid with a faint odour resembling 2 : 4 : 6-trimethylpyridine, and is soluble in 150 parts of water. Dried base completely distils at 203.9° under 771 mm. The constants are : $d_4^{25} = 0.9229$; $n_D^{25} = 1.5084$; $n_C^{25} = 1.5043$; $n_F^{25} = 1.5195$; $n_{G'}^{25} = 1.5290$.

The base was proved to be 2 : 3 : 4 : 6–tetramethylpyridine in the following manner :

0.1027 Gr. base gave 0.0896 gr. H_2O and 0.2993 gr. CO_2. 0.2066 Gr. base gave 18.9 c.c. N_2 at 24° and 762 mm. (Found : C = 79.48 ; H = 9.77 ; N = 10.49 ; mol. wt. = 137. $C_9H_{13}N$ requires C = 79.93 ; H = 9.70 ; N = 10.37% ; mol. wt. = 135.1).

The base (1.04 gr.) was oxidised with 12 gr. of $KMnO_4$; the filtrate from the manganese oxide was concentrated into a small bulk, neutralised with dilute sulphuric acid and treated with a saturated solution of copper acetate. The resulting copper-salt was bluish-green in colour and was ascertained on analysis to be the neutral copper-salt of pyridine-tetracarboxylic acid.

0.1607 Gr. copper salt (dried at 100°) gave 0·0299 gr. H_2O, 0.1383 gr. CO_2 and 0.0549 gr. CuO. (Found : C = 23.46 ; H = 2.08 ; Cu = 27.29. $C_5HN\cdot(CO_2)_4\cdot Cu_2\cdot 4H_2O$ or $C_5HN\cdot(CO_2H)_4\cdot 2Cu(OH)_2$ requires C = 23.99 ; H = 2.01 ; Cu = 28.24%).

The free acid is readily soluble in cold water. A drop of a ferrous sulphate solution on the free acid develops a deep violet colouration, while a dark reddish-purple colour appears when a drop of an acid solution was added inversely to the ferrous sulphate ; sinters at about 190° and melts at 236° with decomposition : these results agree well with those of pyridine–2 : 3 : 4 : 6– tetracarboxylic acid.[1]

(1) O. Mumm and H. Hüneke, loc. cit.

0.1155 Gr. free acid lost 0.0181 gr. on drying at 110° for 2 hours. 0.0971 Gr. dried acid gave 0.0204 gr. H_2O and 0.1471 gr. CO_2. To neutralise 0.1002 gr. of dried acid required 14.8 c.c. of N/10 NaOH. (Found : C = 41.32 ; H = 2.35 ; water of crystallization = 15.7. $C_5HN(CO_2H)_4 \cdot 3H_2O$ requires C = 42.34 ; H = 1.98 ; water of crystallization = 17.6%).

2 : 6 : 4–Dimethyl-ethylpyridine.(1) The fractions b.p. 187°–188° and b.p. 189°–190° were treated with the calculated amount of picric acid in hot alcohol, the mother liquor which separated from the crystals, was left to stand for a long time in an open flask. The brownish-red syrupy picrate filtered from any solid matter which might have been contained in it, gave 20 gr. of free base. The base is a colourless liquid but taking a slight colouring on long exposure to the light, soluble in 160 parts of water at 23°, possesses a characteristic odour of α and γ–methyl-ethylpyridines. B.p. = 187°.5–188°.0 (758 mm.) ; $d_4^{25} = 0.9089$; $n_D^{25} = 1.4964$.

The base corresponds to a parvoline, on analysis, and the oxidation with $KMnO_4$ gives rise to a "trimestic acid" as will be seen from what follows, which compels one of the three side-chains to take an ethyl group. Naturally, we can consider two isomers of such a parvoline according to the position to which the ethyl group is attached, and a close identity in the properties is recognized with 2 : 6–dimethyl–4–ethylpyridine which may therefore be assumed to be the chief constituent of the fraction metioned.

$(C_9H_{13}N \cdot HCl)_2PtCl_4$ . . . . . m.p. 203° (0.1006 gr. subst. gave 0.0290 gr. Pt. Pt found = 28.8, theory = 28.7)

Analysis : 0.0974 gr. base gave 0.0840 gr. H_2O and 0.2850 gr. CO_2. (Found : C = 79.79 ; H = 9.65. $C_9H_{13}N$ requires C = 79.93 ; H = 9.70%).

The base (3.7 gr.) gave 1.0 gr. of free acid on oxidation with potassium permanganate, which becomes a violet-red with ferrous sulphate, and melts at 228°.

Analysis : 0.1296 gr. acid lost 0.0184 gr. on drying at 115° for 2 hours. 0.1000 Gr. dried acid gave 0.0217 gr. H_2O and 0.1660 gr. CO_2. (Found : water of crystallization = 14.20 ; C = 45.28 ; H = 2.43. $C_5H_2N(CO_2H)_3 \cdot 2H_2O$ requires water of crystallization = 14.58 ; C = 45.50 ; H = 2.39%).

Dimethyl-ethyl-pyridine (2 : 3 : 6 ?) From the fraction b.p. 189°–190°, a base was isolated by means of picric acid, which slightly differs from 2 : 4 : 6–parvoline in odour and physical constants. B.p. = 190°–190.5° (764 mm.) ; $d_4^{25} = 0.9107$; $n_D^{25} = 1.4970$.

The base was subjected to partial oxidation to form methyl-ethyl pyridine carboxylic acid which yields by heating with soda-lime, a modicum of 2 ; 6–methyl-ethyl-pyridine.

Analysis : 0.1068 gr. base gave 0.0928 gr. H_2O and 0.3120 gr. CO_2.

(1) F. Engelmann, *Ann.*, **231** (1885), 44 ; *Ber.*, **19** (1886), Ref. 16.

0.1728 Gr. base gave 15.7 c.c. N_2 at 30° and 756 mm. (Found : C=79.67 ; H=9.74 ; N=10.3 : mol. wt.=136. $C_9H_{13}N$ requires C=79.93 ; H=9.70 ; N=10.37% ; mol. wt.=135.1).

When, however, the base was oxidized completely with potassium permanganate, an acid with a m.p. of 245° resulted, which agrees in all respects with 2 : 3 : 6–pyridine tricarboxylic acid.

0.1046 Gr. of the dried acid gave 0.0262 gr. H_2O and 0.1725 gr. CO_2. (Found : C=44.98 ; H=2.80. $C_8H_5O_6N$ requires C=45.49 ; H=2.39%).

Pyrindane. Seeking to find any other compound of the pyridine series such as 3 : 4 : 5–trimethyl pyridine in the last fraction (200°–202°), the writer came upon a peculiar base, which on pursuit with careful examination, of the picrate, was unveiled unexpectedly to be a new and interesting base that has never been found in shale or coal tars, and it would be worthy of note in the sence that it might be a mother substance of the pyrindane series.

The picrate crystallizes from an excess of hot alcohol in flat needles with a m.p. 181°, which was converted into a free base of a hygroscopic, colourless liquid, possessing a faint odour like that of 2 : 3–dimethylpyridine, and one part of the base is soluble in 40 parts of water at 25°. The yield of the base from 9.5 gr. of the salt was 3 gr. The dried base distils completely at 199.8° (761 mm.) and the constants are : $d_4^{25}=1.029$; $n_D^{25}=1.541$; $n_C^{25}=1.536$.

0.1210 Gr. and 0.1169 gr. base gave 0.0813 and 0.0800 gr. H_2O, and, 0.3561 and 0.3442 gr. CO_2 respectively. (Found : C=80.27 & 80.30 ; H=7.52 & 7.66 ; mol. wt.=121. C_8H_9N requires C=80.62 ; H=7.62% ; mol. wt.=119).

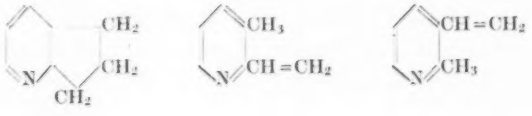
0.1124 Gr. and 0.1747 gr. $(B{\cdot}HCl)_2PtCl_4$ gave 0.0337 and 0.0522 gr. Pt respectively.

Oxidation of base ; 1.0 gr. of the base was oxidised with 9 gr. of potassium permanganate ; the acid formed by the oxidation was converted into a copper salt which showed the characteristic feature of copper quinolinite. The yield of quinolinic acid was 0.8 gr.

0.1048 Gr. free acid gave 0.0284 gr. H_2O and 0.1944 gr. CO_2. (Found : C=50.17 ; H=3.03. $C_7H_5O_4N$ requires C=50.27 ; H=3.02%).

The structural formula for the base would eventually be settled in determining the manners in which the three carbon atoms combine together and are also attached to the pyridine ring :

(I) (II) (III)



From such a point of view the molecular refractivity was first examined. The value calculated from the experimental data shows $M_D=36.34$, while formula I will give $M_D=37.18$, II and III, $M_D=38.89$, in which the specific exaltation ΣE_D is calculated as -0.70 and -2.15 respectively, the latter being considered abnormal. The behavior of the base toward bromine being practically inert at room temperature, is favorable in supporting the structure (I) for the base, and moreover, considering the abnormality in density compared with that of the alkyl-pyridines and the behavior toward the oxidizing agent, such facts seem to compel formula II or III to be rejected.

Some considerations on the boiling-points of the methylpyridines. Although the effect of the methyl group on the boiling-points of certain homologous series, such as the hydrocarbons, alcohols, and acids has been studied by many investigators, there can be little doubt that it is impossible, as conjectured from the stereochemical view point, to contemplate such an attempt in the series of the methylpyridines with all the data hitherto given in the literature. But with the data which the writer has observed throughout the members many regular relations are recognized in them as already stated, if we ascend the series or among the isomers themselves. Convinced that the effect of the methyl group in α–position on the "boiling-point-rise" of the methylpyridines is about half of that of the β– or γ–position throughout the members, yet some anomalies are always found in connection with such members which have methyl groups successively attached unsymmetrically to the pyridine ring. If this is corrected by C the boiling points of the methylpyridnes can be expressed by a fairly simple empirical formula, that is,

$$T=115.3^{\circ} + 14m + 28m' + C$$

where T is a b.p. of methylpyridine, m the number of the α–methyl group m' the number of the β– or the γ–methyl group, and C the correction term.

The correction term C is variable with the position in the pyridine nucleus, by which the methyl groups connected, that is, 4° for the 2.3 ($\gamma:\beta$)-methyls, 8° for the 3 : 4 ($\beta:\gamma$), and these values are diminished to one half if two side-chains are situated in the 1 : 4 positions or para-position.

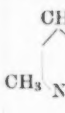
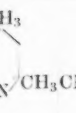
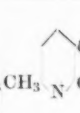
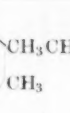
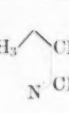
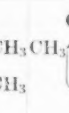
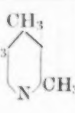
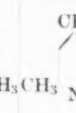
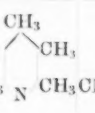
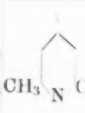
For the methyl derivatives of ethyl-pyridine, 115.3 (b.p. of pyridine) in the above formula should be replaced by the b.p. of ethylpyridine.

In the following table the results of such calculations are given with the author's experimental data in which slight corrections are made in order to compare them under 760 mm.

Physical Constants of Pyridine Series.

B.p. (760 mm.) obs.	115.3	129.3	144.0	145.3	144.0	157.0	158.0	160.8	171.6	178.9
B.p. (760 mm.) calc.	115.3	129.3	143.3	143.3	143.3	157.3	157.3	161.3	171.3	179.3
d_4^{25}	0.9781	0.9400	0.9518	0.9502	0.9183	0.9261	0.9271	0.9419	0.9385	0.9537
n_D^{25}	1.5068	1.4983	1.5038	1.5029	1.4953	1.4982	1.4984	1.5057	1.5032	1.5099
n_C^{25}	1.5022	1.4939	1.4994	1.4986	1.4910	1.4939	1.4942	1.5014	1.4988	1.5055
n_F^{25}	1.5187	1.5097	1.5155	1.5143	1.5065	1.5095	1.5095	1.5172	1.5146	1.5209
$n_{G'}^{25}$	1.5290	1.5197	1.5256	1.5240	1.5164	1.5194	1.5190	1.5272	1.5244	1.5305
M_D	24.04	29.04	28.94	28.95	34.02	33.90	33.88	33.76	33.74	33.58
M_C	23.86	28.82	28.73	28.74	33.77	33.66	33.64	33.52	33.49	33.34
M_F	24.52	29.60	29.51	29.50	34.67	34.55	34.52	34.41	34.38	34.19
$M_{G'}$	24.93	30.09	30.00	29.97	35.24	35.12	35.06	34.96	34.93	34.72
D (G'-C)	1.07	1.27	1.27	1.23	1.47	1.46	1.42	1.44	1.44	1.38
D (F-C)	0.66	0.78	0.78	0.76	0.90	0.89	0.88	0.89	0.89	0.85
ΣE_D	−1.44	−0.90	−1.01	−1.00	−0.43	−0.54	−0.56	−0.67	−0.69	−0.84
Picrate (m.p.)	167	165	149	167	162	167	182	188	244	163
$(B{\cdot}HCl)_2PtCl_4$ (m.p.)	268	205	208	253	211	214	217		263	276
$B{\cdot}HCl{\cdot}AuCl_3$ (m.p.)		181–2	186–7	218						187
$B{\cdot}HCl{\cdot}(X)HgCl_2$ (m.p.)	(X) = (2): 176	(2):153–4	(1):145–6 (2):146 (3):170	(2):130	(1):191.5 (2):167	(6):203	(2):131–2	(6):194		(3):131
Sol. in X pts. of water	any rate (20°)	any rate (20°)	any rate (20°)	any rate (20°)	any rate (20°)	~12(23°)	11.5(35°)	10(23°)	32(23°)	20(22°)

Physical Constants of Pyridine Series. (Continued.)

										
B.p. (760 mm.) obs.	170.3	172.8	186.8	189.8	203.3	160–1	179–80	187.5–8.0	190–.5	199.8
B.p. (760 mm.) calc.	171.3	173.3	187.3	189.3	203.3	162	179	193	190	——
d_4^{25}	0.9101	0.9220	0.9310	0.9330	0.9229	0.9207	0.9130	0.9089	0.9107	1.029
n_D^5	1.4959	1.5018	1.5057	1.5054	1.5084	1.4950	1.4953	1.4964	1.4970	1.541
n_C^{25}	1.4919	1.4976	1.5014	1.5013	1.5043	1.4908		1.4925		1.536
n_F^{25}	1.5069	1.5133	1.5171	1.5165	1.5195	1.5057		1.5071		
$n_{G'}^{25}$	1.5164	1.5232	1.5270	1.5260	1.5290	1.5151		1.5163		
M_D	38.86	38.75	38.62	38.52	43.34	38.36		43.46		
M_C	38.60	38.47	38.35	38.26	43.05	38.08		43.17		
M_F	39.59	39.50	39.35	39.24	44.14	39.06		44.25		
$M_{G'}$	40.22	40.14	39.98	39.84	44.81	39.67		44.92		
D (G'–C)	1.62	1.66	1.63	1.58	1.77	1.59		1.75		
D (F–C)	0.99	1.02	1.00	0.98	1.09	0.98		1.08		
ΣE_D	–0.18	–0.28	–0.38	–0.47	–0.26	–0.60		–0.17		
Picrate (m.p.)	157	148	184	161	107					
$(B{\cdot}HCl)_2PtCl_4$ (m.p.)	220	220	212	192						
$B{\cdot}HCl{\cdot}AuCl_3$ (m.p.)		139								
$B{\cdot}HCl{\cdot}(X)HgCl_2$ (m.p.)	(2):157	(2):104 (6):165	(3):110	(3):112						
Sol. in X pts. of water	34(20°)	38(26)°	66(20°)	50(25°)	150(28°)	55(30°)				

With the expectation that the constituents of the shale tar base boiling at 100°–200° must probably be the mixture of simple pyridine homologues such as the methyl or ethyl-pyridines, the writer has succeeded in isolating seventeen compounds of the pyridine series, three monomethyl pyridines, six dimethyl pyridines, four trimethyl pyridines, one tetramethyl pyridine, two methyl-ethyl-pyridines, one dimethyl-ethyl-pyridine in a highly pure state and in confirming that the theoretically possible isomers of the monomethyl, dimethyl and trimethyl derivatives occur in the shale tar as will be indicated in the table.

1st fraction	(128°–130°)	picoline (main).
2nd „	(143°–145°)	2 : 6–lutidine (main), γ and β-picolines.
3rd „	(157°–160°)	2 : 4–lutidine (main), 2 : 6–collidine, 2 : 3–and 2 : 5– lutidines.
4th „	(170°–172°)	2 : 4 : 6–collidine (main), 2 : 3 : 6–collidine, 3 : 5–lutidine (little).
5th „	(178°–179°)	3 : 4–lutidine, 2 : 4–collidine.
6th „	(186°–190°)	2 : 4 ; 6–parvoline (main), 2 : 3 : 5–and 2 : 4 : 5–collidine, 2 : 3 : 6–parvoline.
7th „	(200°–202°)	2 : 3 : 4 : 6–parvoline, pyrindane.

Thus not only most of the constituents of the shale tar base boiling at 170°–200°, which had been left in the haziness of uncertainty in spite of all endeavours of many investigators, have been cleard up, but also consistent data throughout the members have been determined by rectifying some discrepancies which had crept into the literature.

Besides these pyridine bases, the writer has isolated a new base which has never before been synthesised nor yet isolated from any tars. The base, on analysis and examination of its physical and chemical properties is very likely to have the structure of a "Cyclopenteno-pyridine" and was called pyrindane from its close resemblance in its structure to indane as pyridine to benzene.

The writer desires to make grateful acknowledgment to Vice-Admiral G. Yamashita, Director of the Imperial Naval Fuel Depot, and Engineer Captain Viscount M. Kawase, Chief of the Scientific Research and Experimental Branch for promoting this investigation, and also to Professor S. Komatsu of the Kyoto Imperial University for his invaluable advice and encouragement in carrying out of this research.

The Scientific Research and Experimental Branch,
Imperial Naval Fuel Depot, Tokuyama.

THE HELIUM CONTENTS AND THE AGES OF JAPANESE RADIOACTIVE MINERALS OCCURRING IN ISHIKAWA DISTRICT.

By **Yoshihiko KANO** and **Bunnosuke YAMAGUCHI.**

Received September 12, 1928. Published October 28, 1928.

It is well known that granted certain conditions of suitability, it is possible to calculate the age of a primary radioactive mineral from its contents of uranium, thorium and one of their disintegration end-products, i. e., lead or helium.

There occur in Ishikawa District, Japan, several kinds of radioactive minerals—ishikawaite,(1) samarskite, xenotime and monazite. A series of experiments has been undertaken to determine their contents of helium, from which the authors have calculated their ages. Determining the amount of lead in the ishikawaite, the authors have also estimated its maximum age(2) and compared it with its minimum one calculated from the helium content.

Experimental.

The apparatus employed for the determination of helium is illustrated in Fig. 1. It is similar with that used by the authors for the measurement of helium in the natural gases of Japan,(3) but the whole apparatus is constructed in a smaller size with some suitable modifications. A and B in Fig. 1 show the silica bulbs in which a sample of mineral is heated for the extraction of helium. A is used for dry heating and B for wet treatment of a sample.

As there is a fear of causing an appreciable error in the measurement of a small quantity of helium, if helium is absorbed by cocoanut charcoal cooled by liquid air even at reduced pressure, so the authors have made a preliminary experiment to determine the amount of helium absorbed by the charcoal in the bulb D.

Heating the bulb D to 300°C. by electric furnace, the whole apparatus is exhausted to a vacuum by an oil pump and further by the Töpler's pump F. After cooling of the bulb D, C and D are immersed in liquid air and a definite amount of helium is then introduced into the apparatus from the burette G. The experiment must be carried out with the same care as was

(1) A new kind of uranium mineral was found by Prof. Y. Shibata and named "ishikawaite". [*J. Chem. Soc. Japan*, **43** (1922), 648].

(2) E. Rutherford, "Radioactive Substances and their Radiations", (1913), p. 562, 599.

(3) *J. Chem. Soc. Japan*, **47** (1926), 13 & 452; *Report of the Aeronautical Research Institute, Tokyo Imperial University*, Vol. 1, No. 13 (1926).

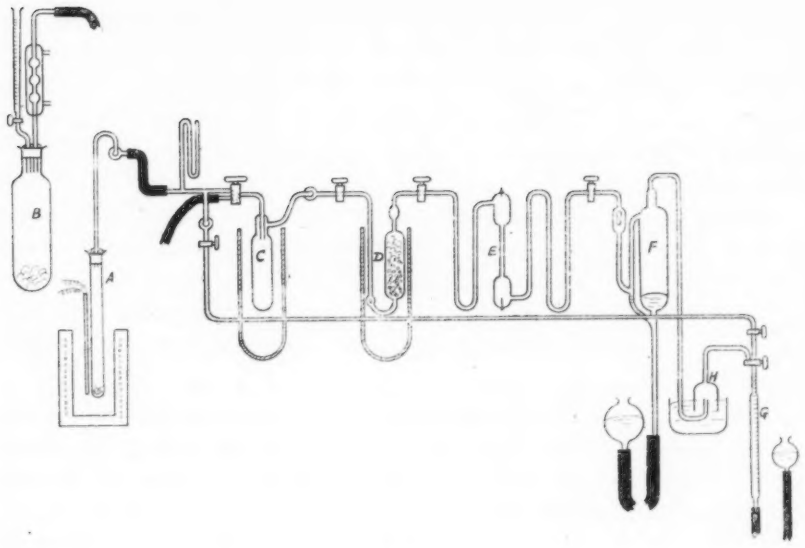


Fig. 1.

taken in the case of analysis of natural gases.[1] Lastly, the helium is drawn over into the adapter tube H by the Töpler's pump F. And as its quantity is measured by the burette G, the amount of helium absorbed by the charcoal in the bulb D can be calculated. Mc Lean[2] observed in his experiment that the amount of helium absorbed by charcoal was so small that it was nearly independent on the quantities of helium introduced into the charcoal bulb. The result of the authors' experiment shown in Table 1, gives the same conclusion.

TABLE 1.

Reaction bulb	Helium introduced (c.c.)	Helium absorbed (c.c.)	Helium absorbed per gr. of charcoal (c.c.)
A (80 c.c.)	0.501	0.041	0.0018
	2.317	0.048	0.0021
	4.891	0.050	0.0022
B (400 c.c.)	0.565	0.038	0.0017
	2.293	0.049	0.0022
	4.812	0.056	0.0025

(1) loc. cit.
(2) *Trans. Roy. Soc. Canada*, **12**, III (1918), 79.

Therefore, in the experiment for the determination of helium present in a radioactive sample, a small amount of helium is previously introduced into the apparatus and after a short time the apparatus is evacuated untill no spark can be passed through the Plücker's tube E. And then, the sample being heated with or without a reacting agent, the helium is evolved and measured in the same manner as above. Powdered samples are used in all the experiments.

Helium in the Ishikawaite. The most radioactive mineral which, like the other minerals, has occurred in Ishikawa District accompanying smoky quartz, microline and biotite in pegmatite layers, has been identified by means of chemical analysis with a mineral named "ishikawaite". It contains 20.86% uranium and 7.5% rare earth elements, possessing a specific gravity 6.3.

The amounts of helium liberated when the sample is heated at 1000°C. and when it is fused with acid potassium sulphate (one part of the sample and 8 parts $KHSO_4$) at 700°C. are given in Table 2, showing that the both methods give a concordant value.

TABLE 2.

Amount of mineral used (gr.)	Method of treatment	Heating temperature (°C.)	Heating duration (hours)	Helium evolved (c.c. at N.T.P.)	Helium per gr. of mineral (c.c.)
2.0013	Mere heating	1000°	2	3.551	1.77
2.0020	One part of the sample is fused with 8 parts of $KHSO_4$.	700°	7	3.483	1.74

TABLE 3.

Amount of mineral used (gr.)	Heating duration at 700°C. (hours)	Helium evolved (c.c.)	Helium evolved per gr. of sample (c.c.)
2.0021	½	3.229	1.613
1.9999	1	3.346	1.673
1.0015	1½	1.701	1.698
2.0005	2	3.448	1.723
2.0000	4	3.465	1.733
2.0020	8	3.483	1.740

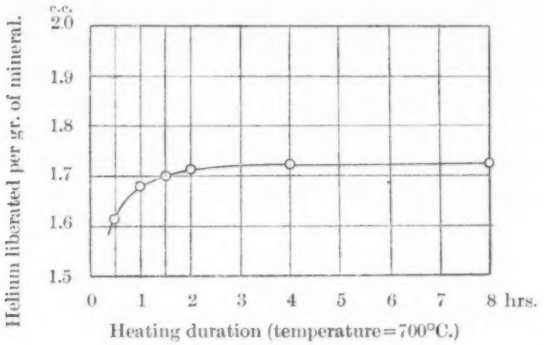


Fig. 2.

Table 3 and Fig. 2 show the effect of heating duration on the liberation of helium when the sample is fused at 700°C. with the same amount of $KHSO_4$ as itself. It is seen that the gas is emitted almost completely after four hours' fusing. If the heating temperature is raised more than 700°C., the rate of liberation of helium increases. This is evident from the results shown in Fig. 3 and Table 4. For the deficiency of the pure sample of ishikawaite, it has been obliged to use a sample somewhat mixed with columbite in this case. The sample contains 14.26% UO_2. Curve I gives the amounts of helium emitted by mere heating of the sample for two hours at various temperatures. On red heat (700–800°C.) the gas in the mineral is liberated nearly by one half but at a temperature higher than 900°C. it is

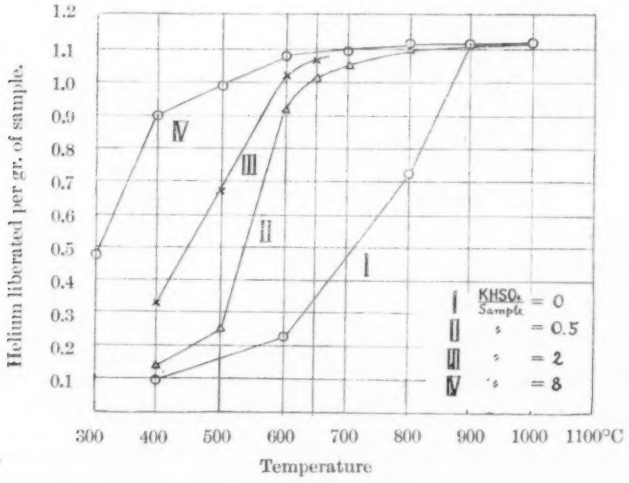


Fig. 3.

given off almost completely. The other curves (II, III & IV) show the quantities of helium evolved when the mineral is fused with $KHSO_4$ at various temperatures, each curve corresponding to each different amount of the fusing agent as noted in the figure. The more the fusing agent is used, the easier the helium in the mineral comes off at any temperature below 900°C. But at 1000°C. the gas in the mineral is liberated completely, independently of the amounts of the fusing agent.

TABLE 4.

Amount of fusing agent	Fusion temp. (°C.)	Amount of mineral used (gr.)	Helium evolved (c.c.)	Helium per gr. of mineral (c.c.)
Mere heating without fusing agent	400	1.4992	0.144	0.096
	600	1.9984	0.472	0.236
	800	1.5011	1.099	0.732
	900	1.3512	1.499	1.109
	1000	1.9992	2.238	1.119
$\frac{KHSO_4}{\text{mineral}} = \frac{1}{2}$	200	1.0003	0	0
	400	1.0003	0.134	0.134
	500	1.0018	0.250	0.250
	600	1.0013	0.919	0.918
	650	1.0001	1.017	1.017
	700	1.0020	1.051	1.049
	800	1.0002	1.100	1.100
	1000	0.9993	1.121	1.122
$\frac{KHSO_4}{\text{mineral}} = 2$	400	1.0013	0.337	0.337
	500	1.0007	0.653	0.653
	600	1.0003	1.050	1.050
	650	1.0003	1.070	1.070
$\frac{KHSO_4}{\text{mineral}} = 8$	200	0.9995	0	0
	300	0.9997	0.480	0.480
	400	0.5004	0.448	0.897
	500	0.5018	0.494	0.984
	600	0.5010	0.542	1.082
	700	0.5003	0.548	1.095
	800	0.5005	0.565	1.129
	1000	0.4994	0.563	1.127

Helium in the Monazite[1] from Ishikawa. The result of experiments on the monazite is shown in Table 5. When the mineral is heated at

(1) J. Sasaki determined the amount of helium which was liberated by this mineral on red heat, and assuming that the quantity was half the whole content of helium, he calculated the age of the mineral (this journal, 1 (1926), 253).

1000°C., it gives off nearly the whole of its helium within several hours, what is found to agree with the result of D.O. Wood's experiment.(1) The helium in the mineral is also liberated almost completely when it is heated with sulphuric acid at a lower temperature for a longer time. Table 6 and Fig. 4 give the temperature effect on the liberation of helium. Five hours' heating at 600°C. makes the sample to give off not more than half the helium present in the mineral, but at a temperature above 800°C. the whole of the gas is emitted for the time.

TABLE 5.

Amount of mineral used (gr.)	Method of treatment	Helium evolved (c.c. at N.T.P.)	Helium per gr. of mineral (c.c.)
4.9991	Heating at 800°C. for 5 hours.	1.115	0.223
3.1254	„	0.725	0.232
3.6709	Heating at 1000°C. for 5 hours.	0.903	0.246
9.9983	Heating at 320°C. with conc. H_2SO_4 for 3 hours.	2.109	0.211

TABLE 6.

Amount of monazite used (gr.)	Heating temperature (°C.)	Heating duration (hours)	Helium evolved (c.c. at N.T.P.)	Helium per gr. of mineral (c.c.)
4.9970	400°	5	0.140	0.028
4.9953	600	„	0.734	0.147
3.1254	800	„	0.725	0.232
3.6709	1000	„	0.903	0.246

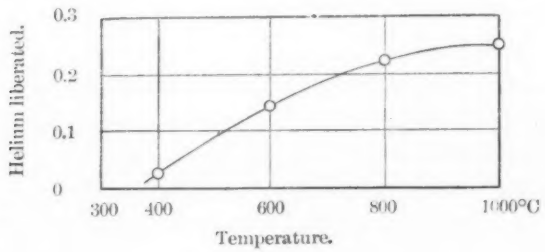


Fig. 4.

(1) *Proc. Roy. Soc. London*, A 84 (1911), 70.

Helium in the Samarskite and the Monazite from Ishikawa. For the liberation of helium in these two minerals, only the heating method is used for the deficiency of the samples. But as the minerals are heated at 1000°C., it may be reasonably acknowledged in view of the results obtained in the cases of ishikawaite and monazite, that each of the minerals loses the whole of its helium.

TABLE 7.

Kind of mineral	Amount used (gr.)	Method of treatment	Helium evolved (c.c.)	Helium per gr. of mineral (c.c.)
Samarskite	3.0011	Heating at 1000°C. for 3 hours.	4.263	1.420
Xenotime	3.2812	Heating at 1000°C. for 2 hours.	0.083	0.025

Calculation of the Ages of the Radioactive Minerals.

The age of a primary radioactive mineral can be calculated from its contents of uranium, thorium and one of their disintegration products, helium or lead. The contents of uranium and thorium in the ishikawaite have been determined by the method of Prof. Y. Shibata,[1] and the amount of lead in the same sample has been measured according to the analytical process outlined in the Table 8. The analysis gives the following result:

Uranium, 20.86% (23.65% as UO_2).

Thorium, nil.

Lead, 0.36%.

For the calculation of the ages of the samarskite and the monazite, the data of Profs. Y. Shibata and K. Kimura[2] on the uranium and thorium contents of the minerals are used.

Samarskite: uranium, 14.87%; thorium, nil.

Monazite: uranium, 0.37%; thorium, 8.50%.

(1) *J. Chem. Soc. Japan*, **43** (1922) 307.

(2) *J. Chem. Soc. Japan*, **43** (1922) 301; **42** (1921), 961.

TABLE 8.

Method of the determination of lead in ishikawaite.

Sample

Fuse 3 gr. of the sample with acid potassium sulphate, and dissolve the fused mass in dil. hydrochloric acid.

Residue — Filtrate

Ignite to expel the residue of hydrochloric acid, fuse with sodium carbonate and dissolve in dil. nitric acid.

Residue — Filtrate

Pass hydrogen sulphide into the solution untill it is saturated, after 2–3 c.c. of a 10% copper solution has been previously added to the filtrate in order to assist the settling of lead sulphide. Wash the precipitate with ammonium sulphide and dissolve it in a hot mixture of hydrochloric and nitric acid. (1 part HCl, 5 parts HNO_3 and 15 parts H_2O). Add 10 c.c. of conc. sulphuric acid, evaporate to SO_3 fumes but not to dryness, add 100 c.c. of water containing 2 c.c. of sulphuric acid and boil. After cooling add 30–40 c.c. of 95% alcohol.*

Residue ($PbSO_4$) — Filtrate

Dissolve in a hot conc. solution of sulphuric acid.

Residue — Filtrate (Pb-acetate)

Acidify the filtrate with acetic acid, add potassium bichromate and boil.

Filtrate — Residue ($PbCrO_4$)

$PbCrO_4$ is weighed in a tared Gooch crucible.

* see W. Scott, "Standard Method of Chemical Analysis". Vol. 1, p. 208.

If (U), (Th) and (Pb) denote the percentage contents in a mineral of uranium, thorium and lead of radioactive origin respectively, the age in millions of years of mineral is given approximately by the formula,

$$\text{Age} = \frac{(Pb)}{(U)+k(Th)}\ C,$$

where k and C are constants, the most trustworthy values of which have been given by A. Holmes and W. Lawson[1] to be: $k=0.38$ and $C=7.400$. The correction may be made for the wearing out of uranium and thorium during the life-time of the mineral, but it can be neglected in the case of relatively young minerals as those from Ishikawa.

(1) *Am. J. Science*, 76 (1927), 327.

Another expression for the age of a mineral by the helium method is given by A. Holmes and W. Lawson, thus

$$\text{Age} = \frac{(He)}{(U)+0.29(Th)} \times 8.5 \text{ million years},$$

where (U) and (Th) denote the percentage contents of the uranium and the thorium in the mineral respectively, and (He), the volume in c.c. of helium at N.T.P. in 100 gr. of the mineral.

According to these formulas the ages of the minerals occurring in Ishikawa have been calculated from the data given in preceding pages.

$$\text{Age of the ishikawaite} = \frac{(He)}{(U)+0.29(Th)} \times 8.5$$

$$= \frac{177.5}{20.85} \times 8.5 = 72.3 \text{ million years}$$

(by the helium method)

$$= \frac{(Pb)}{(U)+0.38(Th)} \times 7{,}400$$

$$= \frac{0.36}{20.85} \times 7{,}400 = 127 \text{ million years}$$

(by the lead method).

$$\text{Age of the samarskite} = \frac{142.1}{14.87} \times 8.5 = 81.2 \text{ million years.}$$

$$\text{Age of the monazite} = \frac{24.6}{0.37+0.29\times 8.5} \times 8.5 = 73.9 \text{ million years.}$$

It is to be naturally expected that the age calculated with lead as an index is greater than the age calculated from the amount of helium present in the mineral. Such is shown in the case of the ishikawaite.(1)

The result of calculation shows that these three minerals from Ishikawa belong to almost a same geological age which must be considered to be Jurrassic or early Crataceous. This consideration is justified by the direct evidence that the pegmatites in which these minerals occur are regarded to belong to the Mesozoic Group.

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(1) Y. Uzumasa gives 29.2 million years as the age of the ishikawaite, determining the amount of lead in the mineral by a colorimetric method, but his value appears to be too small. (see *J. Chem. Soc. Japan*, **48** (1927), 406).

ELECTRODE POTENTIAL OF NICKEL. PART II. EFFECT OF OCCLUDED HYDROGEN ON THE ELECTRODE POTENTIAL OF NICKEL.

By Kwanji MURATA.

Received September 15, 1928. Published October 28, 1928.

In the first paper[1] it was reported that the nickel electrodes which had been freshly prepared from finely powdered nickel oxide by being reduced in hydrogen, and which probably occluded hydrogen, gave an accurately reversible and reproducible electrode potential. But Schoch,[2] and Richards and Behr[3] reported that in their experiment the occluded hydrogen in nickel or iron gave an indefinite and abnormally lower potential. Their results are in conflict with those obtained by the present writer for a nickel electrode. The experiments described in this paper were therefore undertaken with the purpose of deciding whether such occluded hydrogen has actually any considerable effect on the potential or not.

According to Thiel and Hammerschmidt[4] while ordinary nickel does not occlude much hydrogen when it is simply heated in the gas, (0.15 times its volume of hydrogen at 200°C, and 0.68 times at 800°C.), it can take up 11–18 volumes of hydrogen at room temperature under the stimulus of a prolonged cathodic polarization. These values perhaps are not to be taken as absolute but only show the relative absorbing power under varying conditions. Considerable differences have been reported by other observers; these being mainly due to the varying modes and temperatures of preparation and to the conditions of absorption to which it is subjected. Thus, according to Taylor and Burns[5] who made a most thorough study of this subject, some powdered nickel which had been reduced from the oxide at various temperatures absorbed an amount varying from 0.2 to 5 of its volume of hydrogen, decreasing rapidly as the temperature rise. Sieverts[6] has shown that nickel dissolves from 0.18 to 1 volume of hydrogen at the temperatures between 200° and 1000°C., the solubility increasing almost proportionally with increasing temperature, and also that the amount of hydrogen retained by nickel is proportional to the square root of the gaseous pressure.

(1) This journal, **3** (1928), 57.
(2) *Am. Chem. J.*, **41** (1909), 208.
(3) *Z. physik. Chem.*, **58** (1907), 301.
(4) *Z. anorg. allg. Chem.*, **132** (1924), 15.
(5) *J. Am. Chem. Soc.*, **43** (1921), 1277.
(6) *Z. physik. Chem.*, **77** (1911), 591.

Hence the gas absorbed will be given off when the partial pressure is smaller.

On the other hand, Raoult[1] reported that a very porous nickel when polarized cathodically can be made to absorb about 165 times its volume of hydrogen. The amount actually occluded depends on the strength of the current and on the physical nature of the nickel. This extraordinary occlusion of hydrogen is only temporary and the main part of the excess is gradually evolved as the current ceases but the rest of the hydrogen is very tenaciousl yretained by the nickel, forming a kind of solid solution, and can be removed from it only on heating under a reduced pressure. It is well known that electrolytically deposited nickel when heated under reduced pressure gives off hydrogen showing that it, too, occludes hydrogen.

Consequently the first experiment was undertaken in order to find the effect of the hydrogen, produced in nickel by cathodic polarization, on the potential of the nickel electrode.

The second series of experiments was carried out, in an atmosphere of nitrogen in order to determine the effect of the hydrogen occluded by the nickel during its reduction. However, there seemed to be no doubt that the nitrogen used by the present writer was not pure but contained a trace of oxygen owing to the great difficulty in its complete removal, and there is some ambiguity, therefore, in the results of these experiments.

For this reason, the third experiment was carried out in an atmosphere of nitrogen mixed with a little excess of hydrogen over the quantity required to remove the oxygen, with the purpose of deciding the point by comparing the effects of the various concentrations of hydrogen.

Apparatus and Method of Experiment. The electrode vessel and the apparatus for preparing the nickel half-cell were the same as those which served for the former experiments (see "Electrode potential of nickel. Part I," Fig. 1, this journal, 3 (1928), 59). When it was desired to polarize the nickel electrodes with hydrogen, the cell was filled with dilute sulphuric acid which had been stored in one of the reservoirs, H′, and freed from air by passing hydrogen through it, as done in the case of the electrolyte in reservoir H. After the cell had been filled with the acid, as an anode against the nickel electrode a long platinum wire was inserted into the branch tube, f, by releasing the pinch-cock, Q, and through that tube a slow current of the acid solution was allowed to flow freely before and during the course of polarization, in order to prevent any possible diffusion of oxygen into the electrode chamber. After closing the cocks Q and k, the cell having been carefully washed was filled with nickel sulphate solution.

On the other hand, when it was required to work with nitrogen or nitro-

(1) *Compt. rend.*, 69 (1869), 826.

gen with hydrogen added, the cell, after the reduction was completed. was freed from hydrogen through i by an oil pump, the cocks Q and k being closed. The cell was allowed to stand under the reduced pressure for about half an hour and then filled with the gas. The pumping out and filling was repeated several times at 300° C. to remove any hydrogen which might have been occluded by the nickel electrode. In other respects, the procedure was nearly the same as was described in the former paper.

Results of Measurements of Electromotive Force. The combination of the cell was as follows:

$$Ni\,|\,NiSO_4\ (0.05\ M.)\,|\,Saturated\ KCl\,|\,KCl\ (0.1\ N.),\ Hg_2Cl_2\,|\,Hg.$$

In these experiments 0.05 mol $NiSO_4$ was always used and the measurements were made at 25°C. The current always flowed in the cell from left to right.

For the sake of comparison the results obtained in the three series of the experiments are summarised in Table 1. In Fig. 1 are plotted the changes with time of the electromotive forces of these cells.

TABLE 1.

E.M.F. of cell: $Ni\,|\,NiSO_4$ (0.05 M) | Sat. KCl | KCl (0.1 N), $Hg_2Cl_2\,|\,Hg$, at 25°C.

Elapsed time in hours	E.M.F. in volt.				
	Cell No. 5	Cell No. 6	Cell No. 7	Cell No. 7′	Cell No. 8
1	−0.6348	−0.63105	−0.63240	−0.63660	−0.6388
2	−0.6350	−0.63125	−0.63275	−0.63660	−0.6388
4	−0.6353	−0.63130	−0.63345	−0.63655	−0.6387
7	—	—	−0.6338	−0.63655	—
12	—	—	—	—	—
17	−0.6355	−0.6326	−0.6345	—	−0.6385
24 (1 day)	−0.63565	−0.6332	−0.6346	−0.6368	−0.6384
36	−0.63575	−0.6335	−0.6351	−0.6369	−0.6382
48 (2 days)	−0.6359	−0.6337	−0.6354	−0.6370	−0.6380
					H_2 on
60	−0.63600	−0.6339	−0.6355	−0.6372	−0.6379
72 (3 days)	−0.6361	−0.63405	−0.6355	−0.6373	−0.63785
84	—	−0.63415	−0.63545	−0.63725	−0.63780
					O_2 on
85	—	—	—	—	−0.5692
96 (4 days)	−0.6361	−0.6343	−0.6354	—	−0.5868
108	—	−0.6344	−0.6354	—	—
120 (5 days)	−0.6360	−0.6344	−0.6353	−0.63705	—
				O_2 on	
121	—	—	—	−0.5984	—
132	—	−0.6345	−0.6353	−0.6233	—
144 (6 days)	—	−0.6346	−0.6353	—	—
168 (7 days)	—	−0.63455	—	—	—
288 (12 days)	—	−0.6340	—	—	—
		O_2 on			
289	—	−0.5612	—	—	—

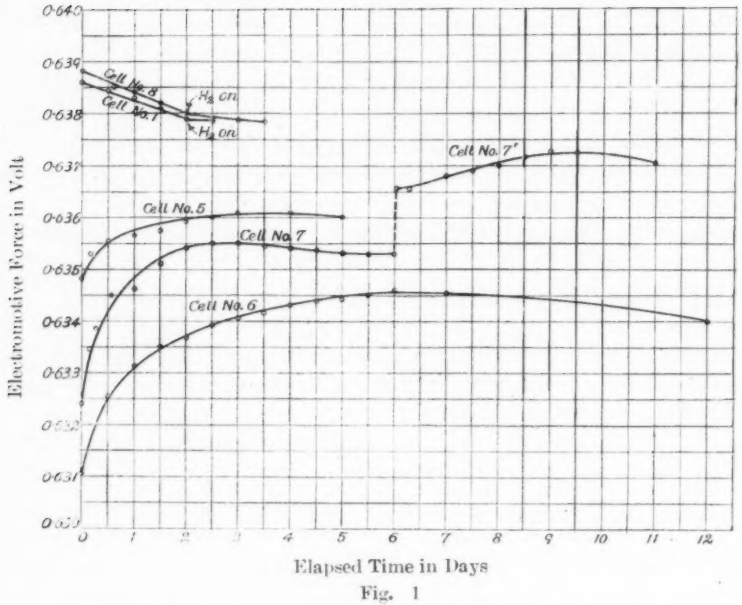

Fig. 1

(*I*) *Effect of the hydrogen produced in nickel by cathodic polarization.* The electrode material in cell No. 5 was prepared exactly in the same way as that in cell No. 1, and it was subjected to cathodic polarization in a decinormal solution of sulphuric acid for five hours with 30 milliampéres at 110 volts. Though the polarization was carefully carried out, the electromotive forces observed with four electrodes in the case of this cell were often found not to agree with each other to a closer precision than ± 0.0005 volt at the beginning of the measurement.

From the results in the case of cell No. 5, as compared with those of cell No. 1, it will be seen that a prolonged cathodic polarization in dilute acid does not cause any increase but rather a slight decrease of the electromotive force, this showing that the results are in conflict with those obtained by previous investigators; i.e. those in the case of the experiments of Schweitzer[1] with the polarized nickel electrode in caustic alkali solution, of Schoch[2] and of others with the nickel polarized in dilute acid or in water, and with the similar experiments of Richards and Behr[3] with iron, and of Schildbach[4] with cobalt, all of which showed that the cathodic polarization

(1) *Z. Electrochem.*, 15 (1909), 607.
(2) Loc. cit.
(3) Loc. cit.
(4) *Z. Electrochem.*, 16 (1910), 967.

caused the increase in the electromotive forces. But, all these previous inverstigators worked under conditions in which there was the possibility that their electrodes might have come in contact with the air during the course of their preparation.

The initial value of the electromotive force in cell No. 5, contrary to expectation, showed a value about 4 millivolts smaller than that in cell No. 1; but this value increased with time to the extent of as much as a few millivolts. At present it is impossible to explain this diminution in the initial value of the electromotive force clearly, but it is supposed that it may be the effect of a trace of the free acid, which might have remained in the cell, owing to the difficulty of the replacing it,—it is impossible to avoid this trouble completely,—especially as the nickel was placed on the platinum wire in the cell as the electrode material, since nickel, which was reduced by the writer's method, evolves hydrogen instantaneously when it comes in contact with sulphuric acid, even when the acid is very dilute. According to the record of the subject, Schoch[1] in his experiments on the influence of free acid on the nickel-calomel cell found that even a trace of it caused a marked decrease in the electromotive force. A similar phenomenon was observed by the author in the investigation of an iron electrode (unpublished).

(*II*) *Measurements in an atmosphere of nitrogen.* The electrode materials in cell Nos. 6 and 7 were prepared in the same way as those in cell No. 1, and then the hydrogen was replaced by nitrogen. In the case of cell No. 6, nitrogen was passed through the electrode vessel for an hour with a speed of two or three bubbles per second (about 50 c.c. per minute) and no repetition was made, while in that of cell No. 7 the method was carried out in the same way as has already been stated. The electrolyte used in both cells was prepared from the same stock solution, and was given as nearly as possible the same treatment.

As the result, for the two cells curves of nearly the same type were obtained as shown in Fig. 1. The initial values of the electromotive forces in both cases were considerably less as compared with that of cell No. 1 and, increasing at first, rapidly arrived at their own maximum values and remained almost constant. There is, however, a considerable difference (1.4 mv.) between the initial values of the two cells, an amount which is too large to be neglected as an experimental error, because the agreement of the individual electrodes of each cell was excellent, and the mean deviation was within only 0.05 mv.

In the case of cell No. 7, after six hours of measurement, the entire solution was removed, the electrodes thoroughly washed, and the cell was refilled with a fresh solution which had been saturated with hydrogen. The result-

(1) Loc. cit.

ing value of the electromotive force measurements increased almost immediately to 0.6366 volt then gradually approached the value of cell No. 1, and finally in three days reached the maximum value of 0.6373 volt where it remained nearly constant. The results given in Fig. 1 are those of cell No. 7′.

The low initial electromotive force of cells Nos. 6 and 7 as compared with that of cell No. 1 may at first sight be attributed to the removal of the hydrogen which had been absorbed by the nickel in the course of reduction. But, such an explanation is inconsistent with the fact that cell No. 7, in which a more complete removal of hydrogen must have been accomplished by the repeated evacuation, did not show a greater lowering of the electromotive force than cell No. 6. This discrepancy led the writer to find the cause in an entirely different direction which is explained as follows.

The nitrogen used in these experiments was obtained by the fractional distillation of liquid air and contains 2–3% of oxygen. It was purified by being passed through three washers of alkaline solution of potassium permanganate, and then through a solid caustic alkali tube, was freed from oxygen by being passed through a combustion tube filled with copper, and was then dried by being passed through a solid caustic soda tube. But, it has been noticed by several workers[1] that by such an ordinary method as was used by the present writer a small amount of the oxygen in nitrogen cannot be completely removed from the nitrogen.

On the other hand, it has already been stated at the beginning of the first paper that even a trace of oxygen greatly affects the potential of nickel. It was actually observed by the writer himself that electromotive forces were almost immediately lowered more than 30 millivolts further by the introduction of a small amount of air after the above measurements had been made. Putting these facts together, it seems very proper to attribute the low electromotive forces in cells Nos. 6 and 7, as compared with cell No. 1, to the effect of the oxidation of nickel occurring during the passage of nitrogen. Then, the higher electromotive force of cell No. 6, as compared with that of cell No. 7, is very well accounted for by the fact that a much larger volume of nitrogen was used in the former and accordingly, a comparatively heavier oxidation took place in it than in the latter.

In the end, this experiment in an atmosphere of nitrogen did not conclusively clear up the effect of the hydrogen contained in nickel on the electrode potential of the metal.

As for the gradual rise of the electromotive force in both cells, a full discussion will be given in the next paper in connection with the mechanism of the reactivation of passive metal.

(1) For example, Kautsky and Thiele, *Z. anorg. allg. Chem.*, **152** (1926), 342.

In the second place, the sudden rise of the electromotive force in cell No. 7′ will be discussed. A sudden rise of the electromotive force caused by the solution saturated with hydrogen in cell No. 7′ seems to have a close connection with the lowering of the electromotive force above explained. Schoch[1] has also observed that in a cell of the same type but with $1N\text{-}NiSO_4$ there is remarkable sudden rise in the electromotive force upon passing hydrogen through the cell, in which all the electrodes used were those which had been kept in air or those that have had a chance of coming in contact with the air. In his experiments the electromotive force was increased by 150 mv. by the passage of hydrogen, reached the abnormally high value of 0.337 volt, and then decreased gradually to the normal value—the electromotive force of the cell with $1N\text{-}NiSO_4$ calculated from the electromotive force for a $0.1N\text{-}NiSO_4$ solution measured by the present writer is 0.276 volt.

From these facts, as compared with the results in the case of cell No. 1 where no appreciable change occured upon the passing of hydrogen, it seems that the introduction of hydrogen causes a marked change in the potential only when the electrode has been previously brought into superficial oxidation by exposure to the air or oxygen, and that the change depends on the degree to which it has been affected.

There is no doubt that the sudden rise in the electomotive force of cell No. 7′ is due to the change on the very surface of the nickel which instantly takes place on its contact with the hydrogen dissolved in the solution. However it is not easy to understand how, under the conditions, such a sudden and remarked change can occur merely as the result of the physical adsorption of hydrogen by the nickel electrode.

Such a change must be considered to be very probably the result of the reduction of the oxide, once formed by the action of oxygen contained in the nitrogen. But the behaviour of hydrogen acting as an electrode must also be taken to into account. The question as to which is the true cause of the sudden change above mentioned was answered by the next experiment which was made in an atmosphere of a mixture of nitrogen and hydrogen with the purpose of clearing up the nature of the effect of the hydrogen contained in nickel on the electrode potential of the metal.

(*III*) *Measurements in an atmosphere of nitrogen with the addition of hydrogen.* The experiment on cell No. 8 was carried out under the same conditions as in that of cell No. 7 with the exception of the atmosphere. The gas used in this experiment was prepared by mixing 9 volumes of N_2 and 1 volume of H_2, which is a little over the quantity required to remove the oxygen contained in the nitrogen, and by passing the mixture through

(1) Loc. cit.

a heated palladised asbestos tube.[1] The electrodes were allowed to stand for about an hour at 300°C., a condition which is considered to be sufficient for the establishment of the equilibrium between the partial pressure of hydrogen in the gas phase and the hydrogen dissolved in the nickel.

At the beginning cell No. 8 gave an electromotive force of just the same high value and also the same type of change as that in cell No. 1 which was prepared in an atmosphere of hydrogen only. By this experiment, it was conclusively shown that the hydrogen dissolved in nickel has no effect on the electrode potential of nickel, because if there were any such effect, cell No. 8 should have given a value intermediate between those of cells Nos. 1 and 6.[2]

Secondly, if, as shown by Smits and Lobry du Bruyn[3] the nickel electrode behaves as a hydrogen electrode in an atmosphere of hydrogen, as is the case with one of platinum, it is expected to produce a change of potential of nearly 0.08 volt, but as a matter of fact this result is not produced. Accordingly, it was confirmed that the sudden rise of the electromotive force of cell No. 7′ by the introduction of hydrogen is due to the activation of the passive surface of the nickel. Further discussion of the mechanism of this activating action will be given in the next paper.

In short, as the result of the foregoing series of experiments the conclusion is reached that the hydrogen occluded by nickel has no effect upon the true electrode potential. For the measurement of the electrode potential of nickel, the complete exclusion of oxygen is the essential requirement and the use of the hydrogen atmosphere facilitates only the fulfillment of this requirement.

In conclusion, the writer wishes to express his great indebtedness to Professor G. Fuseya for his kind direction.

(1) The gaseous mixture was collected on water at 20°C. in a gas holder. Therefore, according to the writer's rough calculation the amount of hydrogen required to remove all the oxygen in the nitrogen and also that dissolved in water in the gas holder was found to be about 8% of the nitrogen. The quantity of oxygen dissolved in water was calculated from the solubility of air in water at 20°C. and the whole volume in the gas holder. No attempt was made to find the concentration of hydrogen remaining in the gas, but from the quantity of the oxygen in the nitrogen it was calculated that the concentration of hydrogen was not more than 5% at most.

(2) If the quantity of hydrogen absorbed by nickel is proportional to the square root of the hydrogen pressure, as reported by Sieverts (loc. cit.), the hydrogen content of the nickel in cell No. 8 must have been less than twenty two hundredths of that in cell No. 1, since the hydrogen content of the gas was less than 5%.

(3) Smits, "Die Theorie der Allotropie" (1921), p. 412; *Proc. Acad. Sci. Amsterdam*, **20** (1918) 394.

Summary.

1. A prolonged cathodic polarization of the nickel electrode in dilute acid and in an atmosphere of hydrogen did not cause any increse, but rather a slight decrease in the initial value of the electromotive force of the cell, Ni | $SiSO_4$ (0.05 M.) | KCl (0.1 N.), Hg_2Cl_2 | Hg. The effect of hydrogen produced in the metals of the iron group by cathodic polarization, i.e. of making the metals less noble as found by previous investigators, was not be repeated in the case of reduced nickel powder. The slight diminution in the initial value of the electromotive force is supposed that it may be the effect of a trace of the free acid which might have remained in the cell, owing to the difficulty of the replacing it.

2. The potentials of the nickel electrode in an atmosphere of nitrogen, and of nitrogen mixed with a little hydrogen were measured. As a result of these series of experiments the conclusion is reached that the occluded hydrogen in nickel has no effect upon the true electrode potential. But, it was observed that in the case of an electrode which has been once affected by oxygen, the effect of hydrogen is very remarkable, and the electrode returns to its active state even at a low temperature.

3. For the measurement of the potential of nickel electrode, the complete exclusion of oxygen is the essential requirement.

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THE IDENTITY OF THE TWO POSSIBLE ISOMERIC METHYL ETHYL β-METHYL-α, γ-DICYANOGLUTACONATES.

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By the previous investigations[1] it was shown that the condensation of $C_2H_5OCH{:}CXY$ with $CHNaX'Y'$, and the condensation of $C_2H_5OCH{:}CX'Y'$ with $CHNaXY$, where X, X′, Y, and Y′ represent negative groups such as CN and $COOC_2H_5$, give the same product, while generally the two compounds corresponding to the following formulae can be expected:

(I) $XYC{=}CH{-}CNaX'Y'$,
(II) $X'Y'C{=}CH{-}CNaXY$.[2]

(1) This journal, **2** (1927), 278; **3** (1928), 219.
(2) Of course such arrangements of the negative groups that make the two formulae identical are out of the question.

Thus the sodium derivatives of the nitrile-esters of dicarboxy-glutaconic acid can not be obtained in two isomeric forms that differ from each other only in the positions of the double union and the sodium atom, but only one of the two is obtainable. It was already studied which of the two possible formulae must be assigned to the actually obtained substance in individual cases.[1]

In order to make clear the mechanism of the condensations of this kind, it was important to know whether the products would prove also to be identical when two isomeric derivatives of β-methyl-dicarboxy-glutaconic acid which differ from each other only in the positions of the double union and the sodium atom were to be formed.

The author previously succeeded in the synthesis of diethyl β-methyl-α, γ-dicyanoglutaconate $C_2H_5OCO(CN)C:C(CH_3)\cdot CH(CN)COOC_2H_5$.[2] This synthetical method was utilized for the preparation of the two possible isomeric methyl ethyl β-methyl-α, γ-dicyanoglutaconates. The condensation of ethyl ethoxy-ethylidene-cyanoacetate (α-cyano-β-ethoxy-crotonate) and methyl cyanoacetate in the presence of sodium methylate must yield the compound with formula (III), while methyl ethoxy-ethylidene-cyanoacetate and ethyl cyanoacetate must produce the compound with formula (IV) in the presence of sodium ethylate.

(III) $C_2H_5OCO(CN)C=C(CH_3)–CNa(CN)COOCH_3$

(IV) $CH_3OCO(CN)C=C(CH_3)–CNa(CN)COOC_2H_5$

But the experiments showed that the products were the same, and this fact was already cited in a previous paper.[3] The experimental data are given in the following pages.

The sodium compounds formed in the above condensations did not tend to crystallise, while the sodium derivative of the corresponding diethyl compound easily crystallised. Only the silver derivatives, which were obtained by double decomposition of the sodium compounds with silver nitrate in the aqueous solution, crystallised in colourless silky needles from hot alcoholic solution. In order to obtain any of the other metallic derivatives in crystalline form, the experiments on double decomposition of the silver compound with potassium, lithium, barium, and mercuric chlorides were tried without success. On concentrating the aqueous solutions none of the compounds of these metals was brought to crystallisation. It was anticipated that the free compounds, methyl ethyl β-methyl-α, γ-dicyanoglutaconates, which might be obtained from the sodium compounds, would be

(1) This journal, **3** (1928), 221.
(2) This journal, **3** (1928), 102.
(3) This journal, **3** (1928), 224.

too easily changeable to be subjected to the processes of identification, for diethyl β-methyl-α, γ-dicyanoglutaconate itself had been found not to be obtainable in a stable form. Thus the author was obliged to compare the properties of the crystals of the silver compounds.

In the experiment of the refractive indices the silver derivatives of the diethyl compound previously prepared, and of the dimethyl compound newly synthesized were studied side by side with the methyl ethyl compounds.

Preparation. Ethyl ethoxy-ethylidene-cyanoacetate $C_2H_5OC(CH_3):C(CN)COOC_2H_5$ was added to the mixture of methyl cyanoacetate and the methyl alcoholic solution of sodium methylate, the quantities of the three substances being in the molecular proportion. The clear yellow solution was evaporated in vacuo over sulphuric acid to a viscous mass, and it was dissolved in water and the theoretical amount of silver nitrate (in aqueous solution) was added. The silver compound was precipitated in white voluminous powder, which was collected, washed with water, and dried in a desiccator. This silver compound was dissolved in hot absolute alcohol, which was filtered while hot and allowed to crystallise. The recrystallisation was repeated several times. A long boiling in alcoholic solution caused a change of the substance, producing insoluble crystals. Therefore a long heating was avoided in the recrystallisation. The silver compound obtained in this way was long silky needles. It was finely pulverised, dried in a desiccator and analysed. 0.2851 Gr. of the substance gave 20.85 c.c. of nitrogen at 23.5°, 752.8 mm.; 0.2595 gr. of the substance gave 0.3618 gr. of CO_2 and 0.0759 gr. of H_2O. (Found: N=8.10; C=38.03; H=3.27. $C_{11}H_{11}O_4N_2Ag$ requires N=8.16; C=38.48; H=3.23%.) (Specimen A) Considered from the mode of condensation this silver compound must have the following constitution:

$$C_2H_5OCO(CN)C=C(CH_3)-CAg(CN)COOCH_3.$$

By starting from methyl ethoxy-ethylidene-cyanoacetate, ethyl cyanoacetate, and an ethyl alcoholic solution of sodium ethylate, and pursuing the same experimental procedure, another specimen with the same composition was obtained. 0.3252 Gr. of the substance gave 23.75 c.c. of nitrogen at 22.5°, 756.4 mm.; 0.3058 gr. of the substance gave 0.4292 gr. of CO_2 and 0.0903 gr. of H_2O. (Found: N=8.14; C=38.29; H=3.30. $C_{11}H_{11}O_4N_2Ag$ requires N=8.16; C=38.48; H=3.32%). (Specimen B) This compound must have the following constitution:

$$CH_3OCO(CN)C=C(CH_3)-CAg(CN)COOC_2H_5.$$

Methyl ethoxy-ethylidene-cyanoacetate had not been known, and was synthesised by the action of ethyl iodide on the silver derivative of methyl acetyl-cyanoacetate. It melts at 76–77°, nearly the same temperature at which the ethyl ester melts.

Equal parts of the specimens A and B were dissolved together in hot absolute alcohol and the solution was cooled. Thus the mixed crystals were obtained. (Specimen C).

The sodium derivative of dimethyl β-methyl-α, γ-dicyanoglutaconate was obtained by the condensation of methyl ethoxy-ethylidene-cyanoacetate with methyl sodio-cyanoacetate. On concentrating the methyl alcoholic solution the product crystallised gradually. The crystalline mass was dissolved in water and transformed into the silver derivative by double decomposition with silver nitrate. It was recrystallised from absolute alcohol. 0.3204 Gr. of the substance gave 24.2 c.c. of nitrogen at 22°, 758.2 mm.; 0.3140 gr. of the substance gave 0.4153 gr. of CO_2 and 0.0762 gr. of H_2O. (Found: N= 8.49; C=36.08; H=2.72. $C_{10}H_9O_4N_2Ag$ requires N=8.51; C=36.47; H= 2.76%.)

The preparation of the diethyl compound was already described in the previous paper.[1] The diethyl and dimethyl compounds are represented by the following formulae respectively:

$C_2H_5OCO(CN)C=C(CH_3)-CAg(CN)COOC_2H_5$,

$CH_3OCO(CN)C=C(CH_3)-CAg(CN)COOCH_3$.

Identification. Photographs of X-ray spectra of the specimens A and B were taken by Debye-Scherrer's method. The lines on the two films coincided entirely. The Kα-line of molybdenum was used. The most intense line corresponded to the lattice distance 3.56 Å. This line can not be attributed to metallic silver which might be produced by the decomposition of the substance on exposure to X-rays, for the lattice distance of the metallic silver is 4.06 Å.

The second method of identification was the comparison of the refractive indices. The crystals of all the three specimens A, B, and C gave the same results. They elongate in the direction of the optical elasticity axis X. Therefore n_1 (refractive index for the faster wave) is equal to α and constant around the zone of elongation. $\alpha_D^{27°}$ was determined to be 1.503 ± 0.001 by the immersion method, and the character of zone was found negative.

The crystals of the dimethyl compound elongate also in the direction of the optical elasticity axis X; n_1 is equal to α, and constant around the zone of elongation. $\alpha_D^{27°}=1.518 \pm 0.002$. The character of zone is negative.

The crystals of the diethyl compound elongate in the direction of the optical elasticity axis Z; the character of zone is positive; and $\alpha_D^{27°}$ was found to be nearly 1.580.

No difference has been found between the specimens A, B and C, and this fact reasonably leads to the conclusion that the specimen A, the con-

(1) This journal, **3** (1928), 104.

densation product of ethyl ethoxy-ethylidene-cyanoacetate with methyl cyanoacetate in the presence of sodium methylate, and the specimen B, the condensation product of methyl ethoxy-ethylidene-cyanoacetate with ethyl cyanoacetate in the presence of sodium ethylate, are identical.

Although it is not yet able to decide whether the constitution of the condensation product is the type (III) or (IV), the condensations can be explained similarly as in the cases of the condensations of ethoxy-methylene compounds with sodio-methylene compounds, the fact that the methyl group in the β-position caused no peculiarity in the condensations being very favorable to this explanation.[1]

The author is much indebted to Dr. I. Okada for photographing the X-ray spectra and measuring the refractive indices.

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(1) See this journal, 3 (1928), 223.